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SEMI-ANNUAL PROGRESS REPORT

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INTRODUCTION

This twelfth semi-annual report from the Interdisciplinary Materials Research program at Rensselaer follows the format established by previous reports. It contains a brief description of the studies that were carried out under each research project during the report period along with some interim results and a description of the studies that are planned for the ensuing six months.

RESEARCH PROJECTS

Mechanical Properties of Polymers 470.05

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A. Fracture of Polymers

Fatigue behavior studies of glassy polymers such as polymethylmethacrylate and polystyrene are now in progress. Theoretical studies are also being conducted in an attempt to elucidate both the initiation and propagation mechanisms for fatigue loading histories. Since such studies require a detailed understanding of localized plasticity and yielding in glasslike polymeric systems, a complementary study on heterogeneous deformation behavior has also been undertaken. Simple shear and simple shear with transverse normal stress load systems are being applied to polymethylmethacrylate samples, and the results obtained from this study should

clarify the role that dilatation and shear play in heterogeneous yielding.

Application of the above studies to the mechanical properties of composite systems is also in progress under a grant from the National Institute of Dental Research.

B. Polymer-Solvent Interactions

Simultaneous absorption and swelling measurements on various solid polymers immersed in active liquid environments have shown conclusively that the gravimetric technique commonly used for the determination of the cohesive energy density of polymers can give misleading results. These experiments have led to the design of a constant volume polymer-liquid interaction cell which is now operational. Several crosslinked and non crosslinked polymers will be studied at constant volume in order to determine true cohesive energy density parameters. Also, the measurements may prove useful to a study of the disorder spectrum of amorphous materials.

C. Other Studies

A minimum free energy network theory previously described has been successfully applied to a rubber network. It has been shown that an affine deformation is the minimum free energy deformation at small strains but that the crosslink deformations are highly non affine at high extensions of the rubber. These results may give clearer meaning to the often measured stress-temperature coefficients of rubbery materials. For example, the minimum free energy approach gives a stored energy function which is a function of more than just the first deformation invariant; thus, it may be possible to give precise molecular meaning to the Mooney correction factor. The behavior of a minimum free energy network of "Langevin chains" is now underway.

Dielectric spectra and x-ray diffraction studies of polyvinyl (alcohol-acetate) copolymers have been completed and will be published in detail in the near future. Also, mechanical spectra studies of these systems are being continued. High pressure x-ray diffraction studies, supported by the National Institute of Dental Research are also being continued.

A Study of the Interaction of Dislocation with the Discrete Second-Phase Particles in Dispersion-Strengthened Alloys

470.09

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The objectives of this program has been to delineate the effects associated with the presence of a distributed second-phase in a crystalline matrix by both theoretical considerations and experimental observations.

During this period, research efforts have centered principally upon experimental observations utilizing both replication and thin film transmission electron microscopy techniques. The specific areas investigated include:

A. Recovery and Recrystallization Kinetics

Recent work in this laboratory has demonstrated that the recovery and recrystallization kinetics of two-phase alloys is controlled by the rate of grain boundary disintegration. Here, dislocations move in and out of the boundary or cell walls, changing the dislocation density and configuration in the boundary structure and hence the degree of misorientation across the boundary. The role of the second-phase in this behavior lies in its interactions restricting dislocation motion through the cell interiors and hence slowing the rates of recovery and recrystallization. In order to determine the generality of this recovery and recrystallization mechanism, studies were initiated of the recrystallization and recovery behavior of high purity aluminum, utilizing hot stage transmission electron microscopy and cine and sequence recording techniques. The initial effort on this study has been directed towards the definition of standard substructural configurations produced by cold work. This portion of the study has been essentially completed and should provide a marker to delineate the progress of dislocation rearrangement during the recovery process. This study is currently in progress.

B. Fracture Behavior

The influence of a distributed phase upon fracture mode and crack propagation is being studied in steel. Replication studies of the fracture surfaces of these alloys broken in fatigue are being used to establish the mechanism by which dissolved gases, particularly hydrogen, affect fatigue fracture. This program is currently in progress and is being handled in cooperation with Dr. H. Rogers of the General Electric Research Laboratory.

C. Precipitation Kinetics

The formation of quench and solute-induced defect structures apparently controls the nucleation and growth kinetics of many precipitate phases. This present study is concerned with the nature of such heterogeneous nucleation kinetics upon precipitation using Al-Ag and Al-Ag-4 alloys as model alloy systems. Currently, this area is being pursued with a dual emphasis on both the formation of the defect structure and the influence

of this defect structure upon the nucleation and growth mechanisms involved in the formation of the α phase. Transmission electron microscopy has shown that several types of defect structures can be generated in these alloy systems, each of which can act in the formation of the α phase. While the final phase morphology is rather insensitive to the origin of phase formation, the initial α nucleation is uniquely defined by the original defect structure. This study is currently in progress.

D. Martensite Transformation

The kinetics of the martensite transformation in the Fe-C system have proved elusive. As a result of recent work in this laboratory, it is felt that this transformation may be controlled by the shear strength of austenite. For this reason an investigation of the kinetics of the martensite transformation as a function of austenite strength has been undertaken.

An apparatus has been constructed which provides for austenitizing steel specimens, quenching to just above the M_s temperature, performing tensile tests at this temperature, and then quenching to form martensite. During the final quenching, the progress of the transformation is followed by continuous magnetic response measurements on the specimen. Thus, the effect of the flow stress of the prior austenite, as modified by work hardening, on the kinetics of the martensite transformation can be determined. This investigation has shown that the M_s temperature is a direct function of the flow stress. This work has now been completed.

Previously, in this laboratory, it was shown that very fast rates of quenching from austenite increased the temperature for the start of the martensite transformation. This work was interpreted as reflecting the degree to which carbon segregated during the quenching process and thereby influenced the shear strength of the austenite. This study now has been extended to Fe-C-x alloys, in order to determine the effects of third elements upon this behavior. Transmission electron microscopy is being used to determine the effects of quench rate upon the structure of the as-quenched martensite.

E. Dispersion-Strengthening

Two studies are being undertaken in order to further elucidate the mechanism by which a dispersed second phase enhances the mechanical properties of crystalline solids.

The first is a study of the influence of particle size, shape, and interface upon the yield strength of these alloys. A series of nickel base alloys containing the Ni_3Al phase has been chosen as model alloy systems for this study. By changing the heat treatment schedule, the shape, size, and interface characteristics of the dispersed phase can be altered. Currently, transmission electron microscopy and replication techniques are being used to quantitatively determine the dispersed phase morphology. After this phase of the program, the mechanical behavior of similarly processed specimens will be determined and the results correlated with the structural data.

The second program deals with a basic hypothesis of the strengthening models which have been proposed to account for the effect of a distributed phase. Is second phase particle shear a requirement for the yielding behavior of an alloy containing a fine distribution of hard particles? A transmission electron microscope investigation in this area has been initiated.

F. Theoretical Studies

Theoretical studies of the strengthening mechanisms in solids based upon dislocation theory are progressing on a continuous basis.

Mechanisms of Solidification 470.10

Senior Investigator: W.J. Childs, Ph.D.
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Research Staff: J.J. Frawley, Ph.D.
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The influence of vibration on grain refinement after nucleation of supercooled alloys of both bismuth and tin has been studied.

Multiplication of grains by remelting of dendrite arms has been demonstrated. The fine dendrite arms formed in tin alloys are rather easily melted and are broken off when vibration occurs giving rise to new grains. The coarser dendrite plates in bismuth alloys are not broken and grain refinement is minimized. Microradiographs have been made of these alloys to study segregation and dendrite morphology.

The initiation of branches in dendrites grown in supercooled metals has been studied for tin, lead and nickel, in decanted specimens. The initiation of branches occurs after a definite amount of growth. This has been related to the Mullins and Sekerka analysis. Branching has been eliminated when the supercooling has been sufficiently high. Growth along the crucible wall has been demonstrated to occur preferentially for many metals and to a degree that can not be accounted for on the basis of the slight temperature gradient which exists. The presence of the containing vessel or the slag interface appears to enhance growth rate and also affect the direction of growth.

Ultrasonic Research 470.11

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The investigation of the elastic constants of anthracene has been brought to a reasonably satisfactory conclusion. Of the thirteen elastic constants which characterize monoclinic crystals, four were determined with

accuracies of a few percent. Larger inaccuracies, from 10 to 100% uncertainties, characterized the values of seven other constants. Two constants C_{13} and C_{25} were completely undetermined because the accumulation of error in the data reduction lead eventually to imaginary values for these quantities.

The work on the beam mixing has proceeded well. With fused quartz blank we have been able to observe "beating down" in frequency as well as the "beating up" reported earlier. This corresponds to induced phonon emission in the language of quantum mechanics. The didactic aspects of these demonstrations of phonon reaction will be explored.

Ultrasonic Pulse Interferometry

470.12

Senior Investigator:	S. Katz, Ph.D. Professor of Geophysics
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The study on metal halides in a pressure gradient, performed as a doctoral dissertation (R.N. Schock), has been accepted for publication and will appear in 1967. Other compounds are being sought which may exhibit similar effects: dissociation in a pressure gradient and subsequent migration of the constituents in opposite directions, depending upon compressibility.

Among the polycrystalline substances for which ultrasonic measurements of the density and elastic constants have been obtained to over 50 kb at room temperature are Al, Co, Cu, Fe, Mg, Mo, Ni and BN, KCl, NaCl, and pyrophyllite. A number of other substances of considerable interest in themselves and for high-pressure applications, including Bi, Pb, PbTe, and AgCl have proven very difficult to study by the present methods. For all the above materials, the bulk modulus varies linearly with pressure, and the Murnaghan hydrostatic equation-of-state describes the density variation to over 50 kb.

Initially powdered, brittle materials show pronounced porosity effects in their elastic properties. Existing theories predict these effects adequately at low pressures. Extension of these theories to higher pressures is under way.

The Relation of Molecular Structure and Intermolecular Action in Flow of Polymers and Polymer Dispersions as a Function of Temperature and Shear Rate

470.15

Senior Investigator:	W.H. Bauer, Ph.D. Professor of Physical Chemistry
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The objective of the research has been to relate the flow properties of liquid polymers related to polybutadienes with the molecular structure and other properties of the polymers.

The flow properties of solutions of polybutadienes are being studied in appropriate solvents.

It is planned to continue the examination of the flow properties of solutions of polybutadienes with the expectation that these properties will be related to the molecular structure.

The Influence of Deformation Mode on the Ductile 470.18
to Brittle Transition of FeCo-V Alloys

Senior Investigator: N.S. Stoloff, Ph.D.
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Current research is exploring the mechanism(s) of stress-corrosion cracking of copper-base alloys in aqueous ammonia. Work by other investigators has indicated that alloy content, stress, grain size, solution pH, and the oxygen and copper contents of the solution are all significant parameters in failures of copper-base alloys by stress-corrosion.

The copper-rich end of the copper-aluminum system is being investigated at a constant grain size with the stress level being maintained at the 0.2% offset yield stress.

Solution chemistry is being varied with respect to copper content, ammonia content, and pH.

Results obtained thus far indicate that time to failure decreases with increasing alloy content and with increasing copper content in the corrosive solution.

While investigations of Cu-30 Zn indicate that a minimum failure time is observed at pH=7, this is not observed in Cu - Al; furthermore, it is observed that time to failure increases logarithmically with decreasing pH in the range 10 to 14.

Low Temperature Physics 470.19

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Ultrasonic attenuation studies of superconducting lead, mercury, and thallium are nearing completion. In this area, experiment is clearly ahead of theory and has recently prompted considerable theoretical activity. It appears that, in the cases of lead and mercury which both have large populations of phonons at their superconducting transition temperatures, much of the anomalous behavior can be explained in terms of a variable electron mean free path. Such an idea has recently been proposed by Ambegaokar and Woo. In our work electron mean free paths have been determined in the normal state which allow calculation of the normal state attenuation and the superconducting mean free paths. This yields considerable improvement in agreement between theory and experiment but, in view of other theoretical efforts of late, does not appear to be unique. Some further analysis will be carried out but, because of the theoretical situation, it appears most appropriate simply to publish trustworthy experimental results in considerable detail.

As a result of earlier work on superconductivity and lattice defects a letter entitled, "Resistance in the Mixed State of Type II Superconductors" by Willis, Schenck, and Shaw will soon appear in Applied Physics Letters. Further work on the model proposed there is being pursued by the principal investigator while on leave at Los Alamos Scientific Laboratory.

Defect studies by ultrasonic attenuation and γ irradiation in lead are continuing. It now appears that vacancies can be created or torn away from dislocations simply by thermal cycling without irradiation. A model has been developed and is presently under test concerning the motion of interstitials along dislocations in lead.

Pyrolytic Materials

470.20

Senior Investigator:	R.J. Diefendorf, Ph.D. Associate Professor of Metallurgical Engineering
Research Staff:	B. Butler, B.S. Graduate Assistant R. Mehalso Graduate Assistant

One of the major aims of materials engineering is to determine the relationship of forming processes to structure to properties of materials. The research funded in this project has been performed to determine these relationships for several materials which are critical to aerospace applications.

Two major areas of effort were studied for the past six months:

1. High temperature Electronic Materials based on boron nitride carbon solutions.

2. Effect of catalysts on the properties, structures, and deposition profiles of pyrolytic graphite.

Some preliminary studies were made on High Modulus Carbon Yarn (Thornel 25).

A. High Temperature Electronic Materials

Graphite and boron nitride have nearly identical crystal structures and lattice constants. Graphite has a small band gap and is essentially metallic in behavior, while boron nitride is one of the best insulators known. Conventional processing techniques have not been able to form ternaries, since at the necessarily high process temperatures, boron carbide, the thermodynamically stable phase, is formed. However, vapor deposition can form such ternaries metastably. It is planned to make these compositions and to study the resulting electronic properties.

B. Effect of Catalysis on Pyrolytic Graphite

The relationship of deposition conditions to structure and properties is rather well understood for deposition of pyrolytic graphite from methane. It is also known that boron trichloride can strikingly alter the deposition rates and structure of pyrolytic graphite.

During the past six months, the effect of boron trichloride and higher hydrocarbons has been studied on the deposition of pyrolytic graphite from methane. The results were that the higher hydrocarbons were as effective catalysts as was boron trichloride. This implies that much of the variability in making pyrolytic graphite may have come from insufficient control of the composition of the natural gas which is normally used as the pyrolysis gas.

Dispersion-Strengthened Materials

470.23

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A paper, entitled "The High Temperature Steady State Creep of Pure Silver and Internally Oxidized Silver Magnesium Alloys" by G.R. Leverant, F.V. Lenel and G.S. Ansell, based on Dr. Leverant's work on this project has been published in the December 1966 issue of ASM Transactions Quarterly.

A program has been started in which an alloy consisting of a dispersion of Germanium Dioxide in silver is produced by two or three radically different methods. These include internal oxidation of a silver-germanium alloy, co-precipitation of a silver and germanium salt with subsequent decomposition of the salts to elemental silver and germanium oxide and possibly internal oxidation of a silver-germanium alloy powder. These

alloys are to be used for the study of the properties of cold worked and recrystallized dispersion strengthened systems. At present, the preparation of the alloys by the various methods is being investigated.

In connection with the study of creep in dispersion strengthened systems, an investigation of the creep of high purity aluminum is underway. In this work, the creep properties of the aluminum at temperatures near its melting point are being correlated with its structure. In particular, the dislocation structure is observed by transmission electron micrography.

Metallic Dissolution

470.25

Senior Investigator: N.D. Greene, Ph.D.
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The object of this program is to determine the effect of variations in composition and microstructure on the corrosion and electrochemical characteristics of iron and low alloy steels.

Multiple correlation analysis has yielded results which permit the prediction of the corrosion rate of an alloy as a function of its minor element content. Phosphorus and carbon are particularly detrimental to corrosion resistance, as in manganese when present in large amounts. Silicon also lowers resistance, while copper is mildly beneficial. Sulfur, chromium and nickel have no effect on corrosion rate in these low alloys.

Corrosion rate is also dependent on the distribution of iron carbide in the microstructure. For example, dissolution rate is increased markedly by decreasing the average pearlite lamellae spacing in a given alloy.

Polarization tests were performed on several alloys to determine the effects of alloy carbon content and microstructure on basic electrochemical parameters. Experimental Tafel slopes and exchange current densities for the cathodic reaction passed through minimum values at intermediate carbon contents, and were influenced by the build-up of corrosion products on the surface with time. Near the eutectoid composition, parameter values increase with average pearlite spacing, and the highest values are observed for the spheroidize-annealed microstructure. Results indicate that these effects are related to the total amount of iron carbide surface area exposed to the solution.

A paper describing the results of these studies is presently in preparation.

Nuclear Magnetic Resonance Research

470.26

Senior Investigator: P.A. Casabella, Ph.D.
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Our work on the antishielding effect of electrons in alkali halides is continuing. The magnitudes of all of the pertinent experimental quantities have been determined for the nuclei of NaCl and NaBr, but the signs of these quantities are still in doubt. New measurements are now being made to determine these signs. In addition, work has been started on measuring the antishielding effects on sodium nuclei in NaF, chlorine nuclei in KCl, and on bromine in KBr. These are the same nuclei investigated in NaCl and NaBr, but by studying them in different environments we hope to test the validity of our earlier results.

X-Ray Scattering

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The x-ray studies of the lattice dynamics of metals and alloys are continuing. The study on single crystals of zinc down to approximately 4° K is near completion. This experimental work has been coupled with an extended calculation of the thermal diffuse scattering corrections for anisotropic crystal systems. This is an extension of similar calculations for isotropic crystals recently completed in the laboratory. Studies of the thermal diffuse x-ray scattering are being initiated to complement the above experimental and theoretical investigations. The real-time, computer controlled full circle diffractometer is presently being checked out prior to full scale application to this work.

Theoretical lattice dynamical studies in conjunction with the experimental work has continued to provide significant results. The x-ray Debye temperature of Ni has been calculated on the basis of force models determined by Birgeneau et al from neutron studies of the dispersion curves. The agreement with the x-ray measurements is substantially improved over that obtained from previous calculations based on a first neighbor Begbie-Born model. Calculations of the x-ray Debye temperature are in progress. These are chiefly based on interatomic force models and on the experimental elastic constants.

A new phase of the lattice dynamics studies was recently initiated with the aid and guidance of Dr. Samuel Katz and with the use of the high pressure and ultra-sonics equipment in his laboratory. This is the study

of the pressure dependence of the elastic constants of the same metals and alloys examined with x-rays. It is expected that this study will yield interesting information on the anharmonic forces. For example, such measurements would provide a good test for the validity of an interatomic force model. On the other hand, by choosing the force constants of an interatomic force model to agree with the measured pressure dependence of the elastic constants, it is possible to calculate the thermal expansion in order to test the model. Furthermore, a knowledge of the pressure and temperature dependence of the elastic constants will allow an estimate of the separate anharmonic contributions to the elastic constants, i.e., volume expansion effects and the explicit temperature dependent contribution. The pressure studies may also be useful in analyzing the elastic constants of Ni in terms of magnetic and non magnetic contributions.

Previous crystal structure investigations are being continued.

Thermal Properties of Polymers

470.29

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A. Thermal Conductivity

A theory of heat conduction in polymers, derived earlier in this study, has been modified to permit more exact analysis of the effects of molecular geometry on the thermal conductivity of amorphous polymers. Experimental testing of the thermal conductivity of oriented polymers is continuing.

B. Heat Transfer in Porous Media

An analysis of the thermodynamics of porous media has been completed which permits, for some cases, a prediction of the thermodynamic properties of a wetted porous medium from the component properties. These predicted properties permit the evaluation of chemical potentials which appear in non-equilibrium, thermodynamic analyses of simultaneous heat and mass transfer in porous media. Experimental work on simultaneous transport phenomena in porous media is continuing. (Supported by the National Science Foundation).

C. Crystallization

Thin section micrographs of polyethylene-terephthalate suggest that under a variety of conditions this material crystallizes in a fibrillar

form, the fibrils being a screw-like lamellar crystal growth. This tentative conclusion is being followed by further experiments on annealed samples using electron microscopy and low angle x-ray diffraction.

D. Cold Drawing

A series of experiments on polypropylene subjected to repeated cold-drawing followed by annealing below its melting point gave the following general results. Annealing after first drawing caused shrinkage and partial recovery of the cold-drawing deformation. The deformation imparted in subsequent drawings could be completely recovered by annealing. Repeated drawing and annealing progressively makes a specimen more rubbery. Experiments on repeated drawing and annealing will continue for the purpose of studying property changes on cold-drawing.

Electron microscope studies on the morphological changes induced by cold-drawing are continuing. (Supported by the Army Research Office - Durham).

Glass and Non-Metallic Materials

470.30

Senior Investigator: J.D. Mackenzie, Ph.D.
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The objectives of this work are twofold: (a) to correlate structures and properties of glasses and other non-metallic solids, and (b) to prepare new non-metallic materials and study their properties.

During this period, research has been carried out on (1) vapor deposition of nitrides, (2) electrical properties of glass-crystal composites, (3) chalcogenide glasses and (4) hardness of glasses. These projects are still in progress and will be continued.

Irreversible Thermodynamics of the Solid State of Linear High Polymers

470.32

Senior Investigator: B. Wunderlich, Ph.D.
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Graduate Assistant

The measurements of the time dependent specific heats of glasses in the transition region are being continued.

The analysis of metastable folded chain polymer single crystals has been developed to a state that it will be possible in the future to determine the parameters density, heat of fusion, and melting point as a function of morphology. Polyethylene and paraffins are being studied presently using the newly built hot-stage.

The melting behavior of polyoxymethylene irradiated in the x-ray beam has shown a distinct dependence on dose. The irradiation destroys the superheating capability of the crystals indicating chain scission.

Ultra-Low Temperature Solid State Physics Research 470.33

Senior Investigator: G.L. Salinger, Ph.D.
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Research Staff: Y.C. Chiang, M.S.
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Graduate Assistant

The object of this program is to measure the thermal properties of magnetic salts below 4°K . A sample of EuS was obtained from IBM and preliminary measurements show that the thermal conductivity varies linearly with temperature. Single crystals of water soluble paramagnetic salts are being grown but it is proving very difficult to obtain large enough single crystals which can be cut as needed. Methods of preparation of compressed powders are being investigated.

A program involving the low temperature thermal properties of polymers is being initiated. Measurements of specific heat and thermal conductivity of amorphous, crystalline, and partly crystalline polymers can lead to information about the morphology of polymers and about the general behavior of disordered solids. In addition there are several research groups here working with polymers. They are interested in the low temperature information and can prepare special well characterized samples. There is very little work going on in this area. Preliminary thermal conductivity measurements on nylon give $T^{1.3}$ dependence below 4°K , indicating that nylon is partly crystalline. The specific heat obeys a T^3 law. Measurements are continuing in amorphous polymers.

The He^3 cryostat constructed on this contract has been used extensively during the past six months to measure the ultrasonic attenuation in superconducting thallium. Temperatures below 1°K are needed in order to determine the background attenuation in the superconducting state. This research is being directed by Dr. Shaw.

Thermal Decomposition of Inorganic 470.35
Coordination Compounds

Senior Investigator: H. Wiedemeier, Ph.D.
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Graduate Assistant

The objectives of this work are to determine thermodynamic and kinetic properties of vaporization processes of transition metal chalcogenides. This will be done on stoichiometric AB compounds and on ternary single-phase mixtures of these compounds.

Poly- and single-crystalline samples of manganese sulfide, selenide, and telluride have been prepared using fusion and chemical transport techniques. The synthesis of single crystals of ternary compounds of defined composition is presently being studied.

The vaporization behavior of MnSe under equilibrium conditions is being studied employing an automatic vacuum-thermo-balance.

The investigation of the solid solution range in the Mn-Cd-S system as a function of temperature indicates the existence of an intermediate compound, which has to be confirmed by other independent measurements.

The above vaporization and phase studies will be extended to other selenides and to selenium-tellurium systems.

Electron-Spin Resonance

470.37

Senior Investigator:

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Assistant Professor of Physics

Research Staff:

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Graduate Assistant

Studies of the paramagnetic vanadyl complex in V_2O_5 -CaO- B_2O_3 glass systems have been continued. When the V^{4+} concentrations are sufficiently low, spectra are structured and the hyperfine components of the interaction between the unpaired electron and the ^{51}V nucleus are observed. Comparison of the observed spectra with recently reported measurements on V^{4+} complexes in Na_2O - B_2O_3 systems indicate that the nature of the paramagnetic complex appears to be the same for both glass systems. That is, the environment of the V^{4+} is that of a distorted octahedral array of oxygens which, in turn, are presumed to be bound to surrounding BO_4 tetrahedral units. Further studies with variations in constituent concentrations are being carried out.

The possibility of observing high concentrations of interstitial molecules produced under intense γ -radiation of alkali-halides at room temperature has been explored, and a series of magnetic resonance and optical studies have been initiated. A correlation between optical and magnetic properties of various interstitial configurations is sought.

Polymer Characterization

470.38

Senior Investigator: F.W. Billmeyer, Jr., Ph.D.
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Research Staff: P. Ghosh, Ph.D.
Research Assistant

The kinetics and mechanism of polymerization and copolymerization have been studied with an initiator system consisting of t-butyl hydroperoxide and sulfur dioxide. This system is unusual in that a peroxide, typical of radical polymerization, is required for the reaction to proceed, but the usual radical inhibitors such as hydroquinone have no effect. Among the monomers studied are methyl acrylate, methyl methacrylate, and isoprene.

Studies have been initiated on the photodegradation of some diene polymers.

Polymer Support

470.40

Senior Investigator: F.W. Billmeyer, Jr., Ph.D.
Professor of Analytical Chemistry

Research Staff: P.J. Livesey, Ph.D.
Research Assistant

A Polymer Characterization facility has been set up and is operational under the supervision of Dr. P.J. Livesey. A major acquisition during the period, a custom-built angular-dependence light-scattering photometer donated by the Du Pont Company, has been optically aligned, checked, and calibrated.

Studies have been initiated on the molecular characterization of polyoctadecene -1, with the objective of determining its molecular dimensions and correlating them with theory.

TECHNICAL PAPERS SUBMITTED FOR PUBLICATION

Wunderlich, B., Melillo, L.

"Surface Recrystallization of Polyethylene Extended Chain Crystals"
Submitted to Science

Hansen, D., Washo, B.

"Molecular Weight and the Thermal Conductivity of High Polymers"
Published in Kolloid-Zeitschrift, Zeitschrift Fur Polymere

Mackenzie, J.D.

"Photoconductivity and Phototropy in Non-Crystalline Solids"
Presented at the International Conference on Radiation Effects
on Solids

Mackenzie, J.D., Frey, W.J.

"Mechanical Properties of Selected Glass-Crystal Composites"
Submitted to Journal of Materials Science

Sternstein, S.S., Cessna, L.C., Jr.

"Fracture in Glasslike High Polymers: I. Theoretical Considerations"
Submitted to Journal of Polymer Science

Sternstein, S.S., Cessna, L.C., Jr.

"Viscoelasticity and Plasticity Considerations in the Fracture of
Glasslike High Polymers"
Published in Fundamental Phenomena in the Materials Sciences

Wunderlich, B., Keller, A., Cormier, C., Machin, M.

"Annealing of Stirrer Crystallized Polyethylene"
Submitted to Journal of Macromolecular Physics

Hansen, D., Crystal, R.G.

"Repeated Cold-Drawing and Annealing of Polypropylene"
Submitted to Journal of Applied Physics

Lenel, F.V., Ansell, G.S., Leverant, G.R.

"The High-Temperature Steady-State Creep of Pure Silver and Internally
Oxidized Silver-Magnesium Alloys"
Published in Transactions Quarterly

Ansell, G.S., Barton, C.J.

"The Influence of a Second-Phase Interface on the Work Hardening
Behavior of an Aluminum-5 Atomic Per Cent Silver Alloy"
Published in Acta Metallurgica

Ansell, G.S., Clough, W.R., Woehrle, H.R.

"Athermal Stabilization of Austenite"
Published in Transactions Quarterly

Ansell, G.S., Kim, H.S., Rogers, H.C.

"Effect of Dissolved Hydrogen on the Fatigue Behavior of an Al-Al₂O₃
SAP-Type Alloy"
Published in Transactions Quarterly

APPENDIX A

Members of Interdisciplinary Materials Research Center Faculty Committee

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F.V. Lenel	Professor of Metallurgical Engineering and Chairman of the Department of Materials
S.S. Sternstein	Associate Professor of Chemical Engineering
J.M. LoGiudice	Administrative Director of the Interdisciplinary Materials Research Center